

Orbital Selective Pressure-Driven Metal-Insulator Transition in FeO from Dynamical Mean-Field Theory

A. O. Shorikov, Z. V. Pchelkina, V. I. Anisimov, and S. L. Skornyakov
Institute of Metal Physics, Russian Academy of Sciences, 620990 Yekaterinburg, Russia
²*Ural Federal University, 620002 Yekaterinburg, Russia*

M. A. Korotin

Institute of Metal Physics, Russian Academy of Sciences, 620041 Yekaterinburg, Russia

In this Letter we report the first LDA+DMFT (method combining Local Density Approximation with Dynamical Mean-Field Theory) results of magnetic and spectral properties calculation for paramagnetic phases of FeO at ambient and high pressures (HP). At ambient pressure (AP) calculation gave FeO as a Mott insulator with Fe $3d$ -shell in high-spin state. Calculated spectral functions are in a good agreement with experimental PES and IPES data. Experimentally observed metal-insulator transition at high pressure is successfully reproduced in calculations. In contrast to MnO and Fe₂O₃ (d^5 configuration) where metal-insulator transition is accompanied by high-spin to low-spin transition, in FeO (d^6 configuration) average value of magnetic moment $\sqrt{\langle \mu_z^2 \rangle}$ is nearly the same in the insulating phase at AP and metallic phase at HP in agreement with X-Ray spectroscopy data (Phys. Rev. Lett. **83**, 4101 (1999)). The metal-insulator transition is orbital selective with only t_{2g} orbitals demonstrating spectral function typical for strongly correlated metal (well pronounced Hubbard bands and narrow quasiparticle peak) while e_g states remain insulating.

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Introduction.— For many years one of the central issues of condensed matter physics is the metal-insulator transition (MIT) in d - or f -elements compounds [1]. The most spectacular examples are pressure-driven transitions from wide gap Mott insulators to metallic state for transition metal oxides. For MnO and Fe₂O₃ (d^5 configuration) metal-insulator transition is accompanied by high-spin to low-spin transition (HS–LS). Recently MIT in those materials was successfully described theoretically by LDA+DMFT (method combining Local Density Approximation with Dynamical Mean-Field Theory) [2] calculations [3, 4].

Iron oxide also exhibits MIT under high pressure. Resistivity measurements showed that FeO becomes metallic at pressures exceeding 72 GPa [5]. Correct description of MIT under pressure in wüstite (Fe_{1-x}O) is crucial in Earth science because iron oxides are believed to be major constituents of Earth mantle.

At ambient pressure and room temperature FeO has cubic rocksalt B1 structure [6]. Below Néel temperature $T_N=198$ K FeO transforms into rhombohedral structure that could be viewed as a slight elongation along cube diagonal of the original cubic structure. Under pressure at room temperature rhombohedral distortion is observed at ≈ 15 GPa and this structure is preserved up to at least 140 GPa [7, 8]. This transformation to rhombohedral structure was believed to accompany long-range magnetic ordering due to increasing of Néel temperature with pressure [9]. However recent neutron diffraction study of wüstite at room temperature under pressure [10] showed the absence of magnetic peaks corresponding to antiferromagnetism. At high pressures and temperatures

($P > 120$ GPa and $T > 1000$ K) FeO transforms into NiAs B8 phase [11].

In contrast to MnO and Fe₂O₃ it is not clear if FeO undergoes HS–LS transition with increase of pressure. Controversial experimental evidences were obtained for this problem. Mössbauer spectroscopy [12] shows that quadrupole splitting appears between 60 and 90 GPa at room temperature. The authors interpreted that as LS diamagnetic state. On the other hand high pressure X-ray emission spectroscopy [13] demonstrates that the satellite feature in Fe $K\beta$ line associated with HS Fe²⁺ state does not disappear up to 143 GPa.

Electronic structure calculations in standard Density Functional Theory (DFT) methods predict an antiferromagnetic metallic ground state [14] in contrast to experimentally observed insulator with an optical band gap of 2.4 eV [15]. The LDA+U method [16] has been successfully applied to investigate strongly correlated transition metal oxides and predicted an insulating ground state in FeO at ambient pressure [17]. Further investigation done by Gramsch et al. [18] for stoichiometric wüstite has showed that using the value of Coulomb parameter U that reproduces experimentally observed energy gap at ambient pressure one can obtain metal-insulator transition in LDA+U calculations for unrealistically high pressures only.

MIT in transition metal oxides with pressure can be successfully described using LDA+DMFT calculations [3, 4]. In the present work we demonstrate that LDA+DMFT method reproduces MIT for FeO with pressure. However in contrast to MnO and Fe₂O₃ MIT is not accompanied by high-spin to low-spin transition and

metallic spectral function is observed only for t_{2g} orbitals while e_g states remain insulating.

Method.— The LDA+DMFT method [2] calculation scheme is constructed in the following way: first, a Hamiltonian \hat{H}_{LDA} is produced using converged LDA results for the system under investigation, then the many-body Hamiltonian is set up, and finally the corresponding self-consistent DMFT equations are solved. The calculations presented below have been done for crystal volumes corresponding to values of pressure up to 140 GPa and room temperature. Since no structure transition has been observed at low temperatures [8] and NiAs phase appears above 1000 K only all calculation were performed for simple NaCl (B1) cubic crystal structure with lattice constant scaled to give a volume corresponding to applied pressure [5]. Ab-initio calculations of electronic structure were obtained within the pseudopotential plane-wave method PWSCF, as implemented in the Quantum ESPRESSO package [19]. Hamiltonians \hat{H}_{LDA} in Wannier function (WF) basis [20, 21] were produced using projection procedure that is described in details in Ref. 22.

The WFs are defined by the choice of Bloch functions Hilbert space and by a set of trial localized orbitals that will be projected on these Bloch functions. The basis set includes all bands that are formed by O-2p and Fe-3d states and correspondingly full set of O-2p, and Fe-3d atomic orbitals to be projected on Bloch functions for these bands. That would correspond to the extended model where in addition to d -orbitals all p -orbitals are included too.

The resulting 8x8 $p-d$ Hamiltonian to be solved by DMFT has the form

$$\hat{H} = \hat{H}_{LDA} - \hat{H}_{dc} + \frac{1}{2} \sum_{i,\alpha,\beta,\sigma,\sigma'} U_{\alpha\beta}^{\sigma\sigma'} \hat{n}_{i\alpha\sigma}^d \hat{n}_{i\beta\sigma'}^d, \quad (1)$$

where $U_{\alpha\beta}^{\sigma\sigma'}$ is the Coulomb interaction matrix, $\hat{n}_{i\alpha\sigma}^d$ is the occupation number operator for the d electrons with orbitals α or β and spin indices σ or σ' on the i -th site. The term \hat{H}_{dc} stands for the d - d interaction already accounted for in LDA, so called double-counting correction. In the present calculation the double-counting was chosen in the following form $\hat{H}_{dc} = \bar{U}(n_{dmft} - \frac{1}{2})\hat{I}$. Here n_{dmft} is the self-consistent total number of d electrons obtained within the LDA+DMFT, \bar{U} is the average Coulomb parameter for the d shell and \hat{I} is unit operator.

The elements of $U_{\alpha\beta}^{\sigma\sigma'}$ matrix are parameterized by U and J_H according to procedure described in [23]. The values of Coulomb repulsion parameter U and Hund exchange parameter J_H were calculated by the constrained LDA method [24] on Wannier functions [22]. Obtained values $J_H=0.89$ eV, $U = 5$ eV are close to previous estimations [18]. The effective impurity problem for the DMFT was solved by the hybridization expansion Continuous-Time Quantum Monte-Carlo method (CT-QMC) [25]. Calculations for all volumes were performed

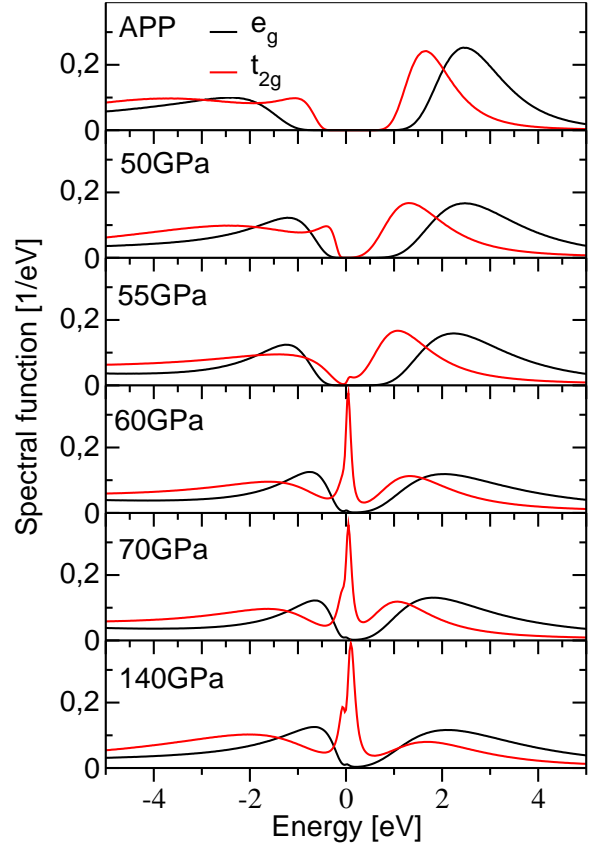


FIG. 1: (Color online) Spectral function of Fe-d states vs. pressure obtained in LDA+DMFT (CT-QMC) calculations at room temperature.

in the paramagnetic state at the inverse temperature $\beta = 1/T = 40$ eV $^{-1}$ corresponding to 290 K. Spectral functions on real energies were calculated by Maximum Entropy Method (MEM)[26].

Results and discussion.— The Fe d band is split by crystal field in triply degenerated t_{2g} and doubly degenerated e_g subbands. LDA fails to describe insulating ground state of FeO at AP and for all volumes FeO is metallic.

Including Coulomb correlation effects in frames of LDA+DMFT method results in high spin state wide gap Mott insulator for ambient pressure phase (APP) of FeO in agreement with experimental data. The calculated energy gap value of about 2 eV agrees well with IPES measurement [27] value 2.5 eV and optical spectrum [15] value 2.4 eV. The occupation numbers for Fe d orbitals are $n(e_g)=0.54$ and $n(t_{2g})=0.68$. The average value of local magnetic moment $\sqrt{\langle \mu_z^2 \rangle}$ is $3.8\mu_B$. Those numbers agree very well with high-spin state of Fe $^{+2}$ ion (d^6 configuration) in cubic crystal field: 2 electrons in e_g states ($n(e_g)=1/2$) and 4 electrons in t_{2g} states ($n(t_{2g})=2/3$) with magnetic moment value $4\mu_B$. Spectral functions $A(\omega)$ for all pressure values calculated by MEM using

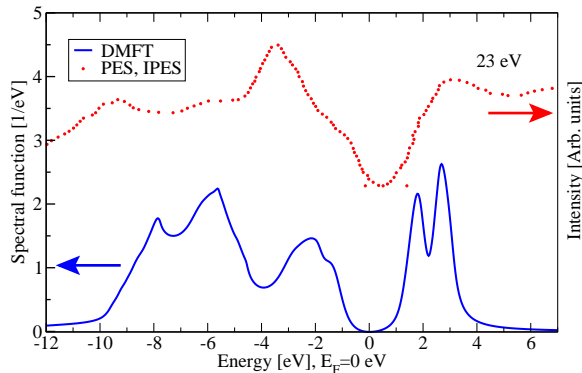


FIG. 2: (Color online) Total spectral function of FeO in ambient pressure phase calculated within LDA+DMFT (CT-QMC) ($\beta=40 \text{ eV}^{-1}$) (solid blue line) in comparison with combined PES and IPES experimental data (red dots) from Ref. [28, 29].

Green function $G(\tau)$ from CT-QMC calculations are presented in the Fig. 1. The spectral function for ambient pressure phase (APP) shows well defined insulating behavior for all d -orbitals. However the energy gap for e_g states is nearly two times larger than for t_{2g} states indicating that the latter orbitals are closer to MIT than the former ones. Figure 2 contains calculated total spectral function compared with spectrum combined from PES and IPES experiments [28, 29]. The theoretical and experimental curves are in a good agreement.

LDA+DMFT calculation made for small volume values corresponding to high pressures gave metallic state for FeO (see Fig. 3) starting from 60 GPa in agreement with experiment [5]. One can see that t_{2g} orbitals become metallic whereas e_g ones remain insulating. This behavior reminds the orbital selective Mott transition (OSMT) in ruthenates [30]. Occupation number values in Fe- d shell are practically not changed comparing with APP and are $n(e_g)=0.55$ $n(t_{2g})=0.68$ at 140 GPa. The magnetic moment value decreases on a few percent only and is $3.5\mu_B$ at 140 GPa. The only interpretation for those values is that an iron d -shell in high pressure metallic phase of FeO still corresponds to high-spin state of Fe^{+2} ion. This conclusion agrees well with analysis of high pressure X-Ray emission spectroscopy experiment made in Ref. [13]. The occupation numbers and magnetic moment vs. pressure are presented in the Fig. 3. One can see that all curves exhibit the kink at 60 GPa. We argue that this feature is due to MIT and corresponding reconstruction of spectral function at Fermi level. Spectral functions $A(\omega)$ for t_{2g} in the Fig. 1 for pressure values larger than 60 GPa become typical for strongly correlated metal close to MIT: well pronounced Hubbard bands and narrow quasiparticle peak. $A(\omega)$ for e_g is still insulating with Hubbard bands only but energy gap value is

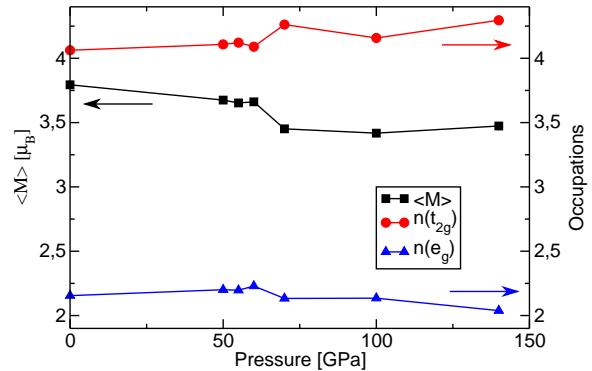


FIG. 3: (Color online) Magnetic moments (black squares) and occupancies of t_{2g} (red circles) and e_g (blue triangles) shells vs. pressure obtained in LDA+DMFT (CT-QMC) calculations.

strongly decreased comparing with APP (see Fig. 1).

To understand these results the following simple model was used. The model has two semicircle DOS of the same width with 3 orbital and 4 electrons. One orbital is non-degenerate and two other orbitals are degenerate. The centers of gravity and DOS widths were taken from *ab initio* LDA calculations. In this model non-degenerate orbital stands for e_g -orbital in FeO and two others for t_{2g} . Occupations in model in HS state are 1/2 for non-degenerate orbital (the same as in realistic LDA+DMFT calculation for FeO) and 3/4 for degenerate orbitals comparing with 2/3 in the case of t_{2g} orbitals in FeO. The Kanamori parametrisation of Coulomb repulsion (with the same $U=5 \text{ eV}$ and $J=0.89 \text{ eV}$) was used. Note, that corresponding matrix elements $U_{\alpha,\beta}^{\sigma,\sigma'}$ (eq. 1) are set to be the same for all orbitals. The model was solved using DMFT (CT-QMC) method and obtained spectral functions for two values of pressure (APP and 140 GPa) are presented in the Fig. 4.

The orbital selective metal-insulated transition (OSMT) was reproduced in these calculations. Since DOSes for all three orbitals have the same width (in contrast to OSMT [30] in ruthenates where two bands have very different widths) and actual structure of DOS is neglected we can conclude that effects of different degeneracy of orbitals and deviation from half filling are the driving force of this separate transition. It is known that critical value of Coulomb interaction parameter U_c needed for metal-insulator transition in half-filled degenerate Hubbard model is $U_c \approx \sqrt{N}U_c^{N=1} - NJ$ [31] (N is degeneracy and $U_c^{N=1}$ is critical U value for non-degenerate case). That means that for more degenerate t_{2g} orbitals one needs larger effective U value to become insulating than for less degenerate e_g orbitals. In addition to that for half-filled states an estimation for effective U_{eff} value is $U + (N-1)J$ while for the occupancy one electron more than half-filling

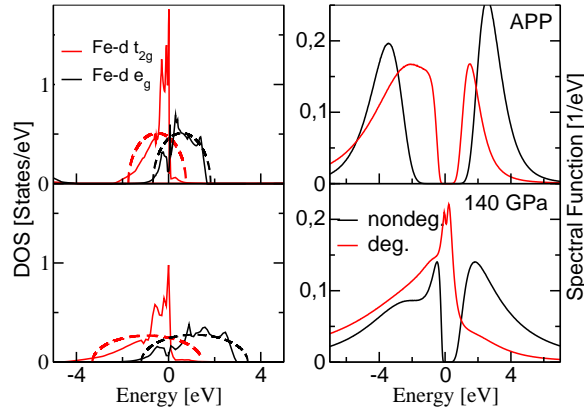


FIG. 4: (Color online) Left panels - LDA densities of states (DOS) (solid lines) and corresponding model semicircle DOS (dashed lines). Right panels - spectral functions from model DMFT (CT-QMC) calculations for two values of pressure. Non degenerate orbital (black lines) reproduces e_g -orbitals and 2 times degenerate one reproduces t_{2g} orbitals (red line).

an estimation is $U_{eff} = U - J$. Then for 2/3 filled t_{2g} orbitals one needs much larger U value to drive them into insulating state than for half-filled e_g states.

In conclusion.— We have performed LDA+DMFT calculation for FeO at room temperature and values of pressure from the ambient one till 140 GPa. In the agreement with experiment spectral function for FeO at AP demonstrates an energy gap of about 2 eV. At the pressures higher than 60 GPa FeO is metallic but only for t_{2g} orbitals while e_g states remain insulating that corresponds to orbital selective Mott transition scenario. The MIT obtained in our calculations is not accompanied by change of spin state and FeO has HS with large local moment in APP and all HPP. This result agrees with high pressure X-Ray emission spectroscopy data.

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